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SURVEY REPORT

PPM MOBILE PCB DESTRUCTION FACILITY PETRO-CANADA REFINERY OAKVILLE APRIL, 1987

ARB-137-87

DECEMBER 1987

Ontario Ministry of the Environment

E. PICHÉ, Director
Air Resources Branch

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- prepared for -

The Central Region

Ontario Ministry of the Environment

- prepared by -

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DECEMBER 1987

Executive Summary

On April 7,8,13 and 14, 1987, the mobile Trace Atmospheric Gas Analyser (TAGA) unit of the Air Resources Branch conducted an air monitoring survey at the Petro-Canada Refinery in Oakville, Ontario. The survey objective was to provide on-site, real-time measurements of ambient PCBs during the testing of a mobile PCB destruction unit operated by PPM (Canada) Incorporated.

During the three days of monitoring a total of 240 2-minute air samples were screened for selected PCBs using the Ministry's TAGA (3000) unit. None of the 16 1/2-hour averaged concentrations for PCBs exceeded the Ministry's 1/2-hour guideline of 0.45 ug/m^3. In fact, all of the measurements for ambient PCBs were below the TAGA's average detection limit of 0.11 ug/m^3 for total PCBs.

Résumé

Les 7, 8, 13 et 14 avril 1987, une unité mobile d'analyse des gaz atmosphériques à l'état de trace, appartenant à la Direction des ressources atmosphériques, a effectué l'analyse de l'air à la raffinerie de Petro-Canada à Oakville (Ontario). Cette analyse visait à fournir des mesures sur place en temps réel des BPC présents dans l'air ambiant au cours d'une mise à l'essai d'une unité mobile de destruction des BPC de PPM (Canada) Inc.

Au cours des trois jours pendant lesquels s'est déroulée l'analyse, la concentration de BPC a été mesurée à l'aide de l'unité mobile d'analyse (modèle 3000) dans un total de 240 échantillons d'air prélevés sur une période de 2 minutes chacun. Aucune des concentrations de BPC relevées sur une moyenne de 16 heures et demie ne dépassait la ligne directrice du Ministère pour une période d'une demi-heure, soit 0,45 ug/m^3. En fait, au cours des analyses, toutes les concentrations de BPC étaient inférieures à la limite moyenne de détection de l'unité mobile, à savoir 0,11 ug/m^3 pour l'ensemble des BPC.

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Introduction

As requested by the Oakville District Office of the Central Region, the mobile Trace Atmospheric Gas Analyser (TAGA 3000) unit of the Air Resources Branch conducted an air monitoring survey in Oakville during the week of April 7, 1987. The purpose of the survey was to provide, on-site, ambient concentration measurements of selected PCBs in the vicinity of the mobile PCB destruction unit operated by PPM (Canada) Incorporated.

PPM had been contracted by Petro-Canada's Trafalgar refinery to decontaminate several transformers and storage tanks containing PCBs at concentrations in the hundreds of parts-per-million (ppm) range. This was the first commercial operation in Ontario of the PPM mobile PCB destruction unit.

The process employed by PPM is based on the well-known reaction of metallic sodium with chlorinated biphenyls. Contaminated oil is pumped into a reaction vessel (tank) where it is mixed with sodium and naphthalene. After the PCB level has been reduced to a concentration of less than 2 ppm, the oil is transferred to a storage tank. Both the reaction tank and the storage tank vent to the atmosphere via a short pipe. All emissions from these tanks pass through a charcoal filter and an oil de-mister.

The mobile TAGA unit was present during the first day (April 8) and the last two days (April 13,14) of operation of the PCB destruction unit. Although the PCB destruction unit was operational on other days, it was on these days (April 8, 13, 14) that PPM was treating oils containing the highest concentrations of PCBs (~200ppm). As the monitoring results became available they were conveyed by the TAGA operators to Bob Graham of the Oakville office. This report summarizes both the analytical protocol and the findings obtained by the mobile TAGA during the destruction of PCBs by PPM at the Petro-Canada refinery in Oakville in April, 1987

2.0 TAGA TECHNOLOGY AND SURVEY STRATEGY

A detailed description of the PCB monitoring technique is provided in Appendix A. Briefly, the TAGA (model 3000) is a specialized quadrupole mass spectrometer with an atmospheric-pressure, chemical ionization (APCI) ion source. To monitor PCBs the ion source is coupled to an Automated Short Term Adsorber (ASTA), which is simply a PCB preconcentrator and thermal desorption device. The TAGA/ASTA technique provides ambient PCB measurements in 2-minute intervals, with a 1/2-hour averaged concentration being computed by averaging 15 consecutive 2-minute samples. In this study, air was screened for the di-, tri-, tetra- and pentachlorobiphenyl isomer groups

Essentially the survey strategy for the mobile TAGA was to position the vehicle immediately downwind of PPM's PCB destruction unit. The ambient PCB levels were then determined every 2 minutes and compared to previously completed background, or upwind, data. Occasionally the survey strategy was modified to compensate for inaccessibility and wind shifts. To ensure that samples were extracted from points approximately downwind of the main emission point, a sampling funnel was attached immediately below the emissions vent located on the reaction tank. Approximately six metres of plastic sampling hose (4 cm inner diameter) connected the funnel directly to the TAGA inlet.

Prior to the start of the PCB destruction process, the TAGA was calibrated for PCB detection and background data were acquired. The background data were used to correct the downwind measurements, and to determine the daily detection limits. (The detection limit (DL) per isomer group is defined as 3 times the standard deviation of the background or upwind signal, observed at the PCB masses, divided by the sensitivity factor. Thus the DL is a function of the TAGA response per unit ug/m^3 and the variation in background signals.) Detection limits for total PCBs monitored (di- to penta-) for the individual days were as follows: April 8 (0.16 ug/m^3), April 13 (0.10 ug/m^3), and April 14 (0.08 ug/m^3). As well, calibrations were randomly conducted to confirm the daily sensitivity factors.

3.0 RESULTS AND DISCUSSION

April 7

The mobile TAGA unit arrived at Petro-Canada's Trafalgar refinery at 10:00 hours, April 7, 1987. Due to the late arrival of one of the PPM rigs it was decided that no PCBs would be destroyed on this day. One calibration was performed on the TAGA to confirm the instrument's sensitivity.

April 8

At 10:30 hours on April 8, 1987, the TAGA began monitoring PPM's process of PCB destruction. To compensate for inaccessibility and to ensure that air samples were collected downwind of the main emission point, a sampling funnel was placed just below the emission vent of PPM's destruction unit. Six metres of plastic sampling hose (4 cm inner diameter) connected the funnel directly to the TAGA inlet.

As seen in Table #1, between 11:00 and 12:36 hours, three (3) 1/2-hour averages indicated that there were no PCBs present above the TAGA detection limit. In fact, PCBs were not detected above the detection limit of .16 ug/m^3 in any of the 45 individual 2-minute air samples. (Recall that a 1/2-hour averaged concentration consists of 15 2-minute air samples.) Following the completion of the second 1/2-hour average the TAGA crew was notified that PPM had completed the destruction of PCBs for this day. A calibration was performed and background data were acquired on site by the TAGA before the crew departed for the day.

April 13

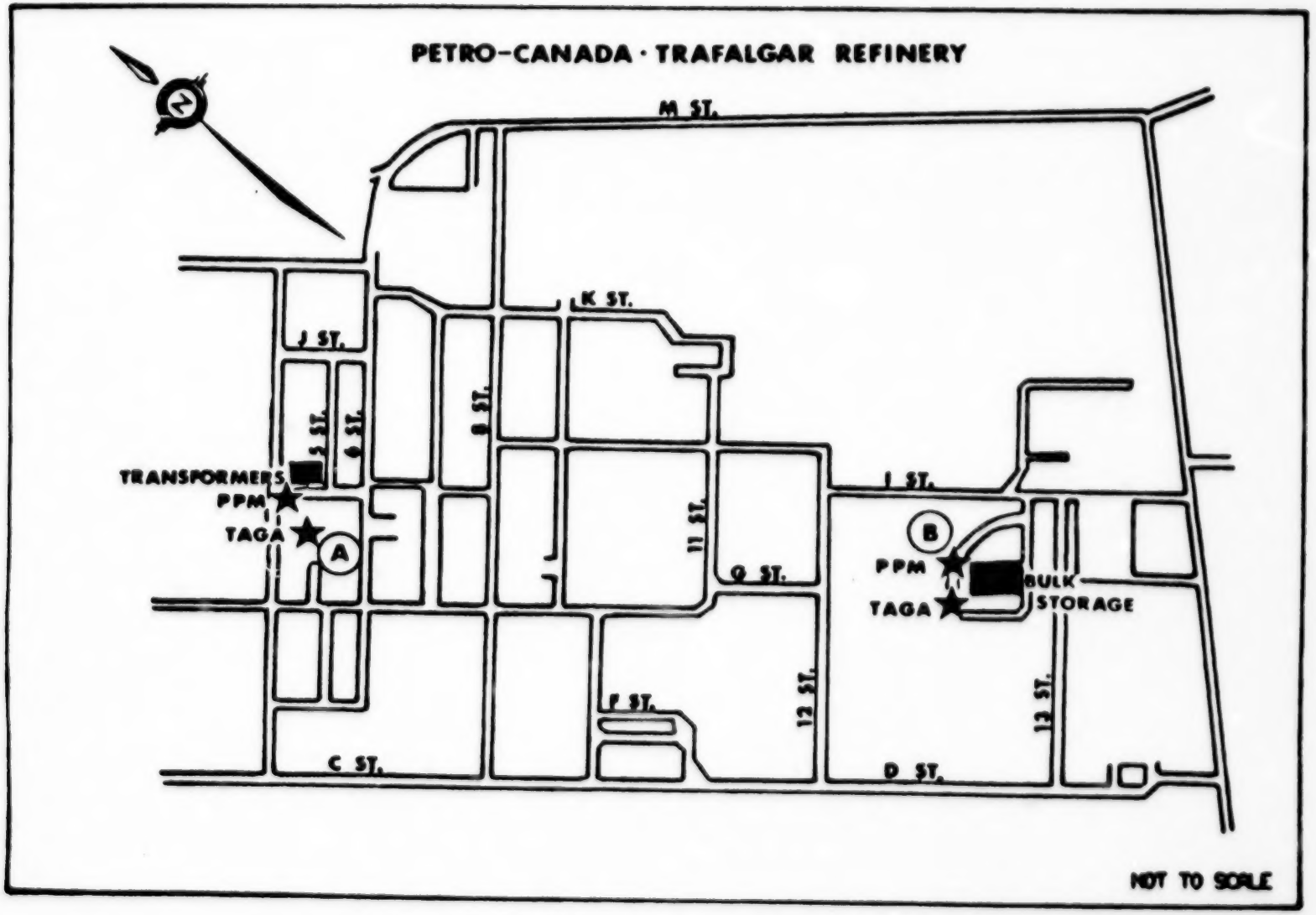
The TAGA returned to the Trafalgar refinery on April 13, when PPM began the decontamination of the oil contained in bulk storage tanks. Of the tanks which were decontaminated, these contained the highest concentration of PCBs (approximately 250 ppm). All monitoring on this day was conducted at Site B (See Map #1).

A total of ten (10) 1/2-hour averages were recorded from 10:55 to 18:38 hours. Of the ten 1/2-hour averages, the first six (10:55 to 15:14 hours) were collected prior to the destruction of PCBs. The first 1/2-hour sample gathered during the destruction of PCBs began at 15:29 hours and, due to a wind shift, the hose and funnel were used to transfer the air samples in the vicinity of the reaction tank directly to the TAGA inlet. Following the first half-hour sample, the wind

speed decreased, making the hose and funnel unnecessary for the next three (3) 1/2-hour averages recorded from 16:50 to 18:38 hours. At no time on this day were PCBs detected above the TAGA's daily analytical detection limit of 0.10 ug/m^3.

April 14

Both the location of the TAGA and the PCB destruction unit were the same as the previous day. Between 10:45 and 12:23 hours the TAGA collected three (3) 1/2-hour averages, none of which required the use of the hose and funnel. As with all of the data gathered during this survey, PCBs were not detected above the TAGA's daily analytical detection limit (0.80 ug/m^3). At 12:55, hours PPM notified the TAGA crew that operations were to cease and thus the air monitoring survey was halted.



Map 1: TAGA Monitoring Locations
Petro Canada (PCB) Survey 1987

TABLE 1: TAGA PCB SURVEY
PETRO-CANADA TRAFALGAR REFINERY, OAKVILLE APRIL, 1987

SAMPLE	DATE	START[1] TIME	MET[2] WS	MET[2] WD	MET[2] AT	LOCATION[3]	½ HR. AVERAGE[4]	COMMENTS
1	8/4/87	11:00	3-12	N	12	SE OF MEROX PIT (A)	ND[5]	DURING PCB DESTRUCTION[6]
2	8/4/87	11:32	-	-	-	SE OF MEROX PIT (A)	ND	PCB DESTRUCTION HALTED AT 11:37[6]
3	8/4/87	12:04	-	-	-	SE OF MEROX PIT (A)	ND	BACKGROUND, AFTER PCB DESTRUCTION
4	13/4/87	10:55	10-25	E	12	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
5	13/4/87	12:33	0-10	SSE	13	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
6	13/4/87	13:05	0-10	SSE	13	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
7	13/4/87	13:37	0-5	SE	13	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
8	13/4/87	14:10	0-5	S	13	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
9	13/4/87	14:42	0-10	S	15	SE OF STORAGE TANK #72 (B)	ND	BACKGROUND, PRIOR TO PCB DESTRUCTION
10	13/4/87	15:29	0-10	S	15	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION[6]
11	13/4/87	16:50	0-10	ESE	12	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION
12	13/4/87	17:34	0-5	ESE	11	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION
13	13/4/87	18:06	0-5	E	10	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION
14	14/4/87	10:45	10-15	E	7	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION
15	14/4/87	11:17	10-15	E	7	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION
16	14/4/87	12:21	10-15	E	8	SE OF STORAGE TANK #72 (B)	ND	DURING PCB DESTRUCTION

NOTE:
1. Start time refers to the adsorb time of the first sample.
2. MET = Meteorological data; WS = wind speed range (km/hr); WD = predominant wind direction; AT = ambient temperature (°C).
3. All monitoring locations were located on Petro Canada property (See Map 1).
4. ½-hour concentration of gaseous PCBs (di to pentachlorobiphenyls); mean of 15 2-minute samples.
5. ND = not detected above the detection limit. (The detection limits were 0.16 $\mu g/m^3$ on April 8, 0.10 $\mu g/m^3$ on April 13, and 0.80 $\mu g/m^3$ on April 14.)
6. Due to inaccessibility, a funnel was employed to acquire downwind data.

Appendix A ... TAGA Methodology for PCB Monitoring

TAGA METHODOLOGY

In 1979 the Air Resources Branch of the Ontario Ministry of the Environment acquired a mobile Trace Atmospheric Gas Analyzer (TAGA 3000) manufactured by Sciex Incorporated of Thornhill, Ontario. The mobile TAGA unit (MAMU No. 3) has been applied to a variety of air monitoring situations, including airborne PCBs. The Ministry has conducted over 50 air quality surveys with the mobile TAGA unit.

The TAGA 3000 is a highly specialized quadrupole mass spectrometer coupled to a unique sampling inlet and ion source (See Figure A1). Ionization of pollutants is achieved through chemical ionization, initiated by a stable corona discharge operating at atmospheric pressure. Since the ion source permits continuous, direct, air sampling at a high flow rate (100 l/min), it is possible to determine the temporal and spatial distribution of selected pollutant levels. The mobile TAGA's capabilities are especially suitable for plume tracking; that is, tracing a pollutant back to its source of origin.

When equipped with the standard atmospheric-pressure chemical ionization (APCI) source the TAGA system is sensitive to most volatile compounds containing a heteroatom, such as N,O,S,P and halide. Typical detection limits are in the range of 0.1 to 10 ug/m3 depending on the type of chemical measured and the sample matrix.

The mobile TAGA unit is also equipped with a 10 metre, telescopic tower and meteorological instrumentation to measure local wind speed, wind direction and ambient temperature. All meteorological data are stored by the on-board computer simultaneously with the collection of air quality data. The data are instantly displayed on the CRT unit allowing the operator to assess the data on-site and thus formulate the appropriate survey strategy.

PCB MONITORING METHODOLOGY

For most chemical classes the sensitivity of the TAGA is extraordinary for ambient air monitoring. However PCBs are one of the exceptions, because the absolute sensitivity is insufficient for instantaneous real-time detection relative to the low guideline set by the Ministry for PCBs ($0.45 ug/m^3$). Thus in the late 1970's Sciex Inc. developed a simple sampling device to preconcentrate volatile PCBs. Preconcentrating the PCBs for only 2-minutes lowers the detection limit by two orders of magnitude.

Although the basic principles have remained unchanged, today's PCB preconcentrator has evolved into a portable sampling inlet system with all operating parameters under strict computer control. It is commercially known as the Automated Short Term Adsorber or ASTA.

The ASTA, shown in Figure A2, consists of two sample probes formed by coiling a nichrome wire, coated with a gas chromatographic stationary phase, OV-17. The positions, and thus functions of the two probes, are interchangeable between the adsorption or sampling position, and the desorption or analysis position. While one probe is adsorbing PCBs from the ambient air, the other probe is being desorbed and analysed for PCBs from a previous air sample. Altering the positions of the two probes permits continuous screening of the ambient air in 2 minute intervals. There is approximately an eight second delay between sampling periods due to the probe cycling time. Thus a "1/2-hour sample", which consists of 15 consecutive 2 minute samples, takes 32 minutes.

Sampling

When sampling for PCBs the probe is placed directly in the ambient air stream (1.7 l/s) for a period of 2 minutes. The probe is then changed to the desorb position and 12 volts DC potential (3.25 amperes) is applied to the probe for a period of 40 seconds. This causes the probe temperature to rapidly increase to approximately 300 °C, thereby transferring the PCBs from the OV-17 into the gas phase. The carrier gas, which is a mixture of ultra pure zero air and benzene (100 ppm), constantly sweeps the PCBs into the ion source. Upon entering the ion source the PCBs immediately undergo benzene chemical ionization, producing molecular PCB ions (M+) which are (mass) selectively monitored by the quadrupole mass filter.

The software allows for the screening of 4 PCB isomer groups

at 8 masses, 2 isotopes per isomer group. Normally the dichlorobiphenyl to pentachlorobiphenyl species are monitored. There are several reasons for this: firstly, the TAGA is more sensitive to these species. Secondly, PCBs with lower molecular weights generally exhibit higher vapour pressures, thus increasing the likelihood of gas phase detection; and, thirdly, in previous PCB surveys the higher molecular weight PCBs were rarely detected when the lower molecular weight PCBs were not observed.

Calibration

Calibration of the system, including sampling probe adsorption efficiencies and TAGA response. is accomplished by continuously injecting known amounts of PCBs directly into the air sampling stream. The PCBs are injected via a heated injection port (300 'C) using a gas-tight syringe and motorized syringe drive. The PCB standards are prepared by the dissolution of pure PCB congeners, one per isomer group, into iso-octane. Repeated injections at 5 different syringe drive settings establishes a calibration curve which is linear (correlation coefficients are usually better than 0.995) over the PCB concentration range of 0.425 to 2.5 ug/m^3 per isomer group (See Figure A3). The relative standard deviations for multiple injections of PCB standards are typically better than 5% at the 0.425 ug/m3 level.

DATA PROCESSING AND INTERPRETATION

Immediately following a desorption of the probe, the TAGA computer calculates the level of PCBs (or equivalents) per isomer group, from the net signal (sample minus background) and the daily calibration factors. In fact, for each PCB isomer group, two measurements are made: one for the chlorine 35 isotope (M), and one for the corresponding chlorine 37 isotope (M+2).

Criteria

At this stage the field survey scientist interprets the reduced data using the following criteria:

1) the adsorption peak (integrated signal) must be as least 3 times greater than the signal noise (S/N>3);

2) the PCB levels for a given isotope pair must be within the overall experimental accuracy of 20%;

3) the calculated isotope ratios must be within 10% of the theoretical isotope ratio for a given isomer group.

If condition 1) above is not satisfied, the isomer group concentration will be considered below the detection limit and a ND is reported. If conditions 2) and 3) are not evident then a chemical interference at one, or both, of the isomer groups is assumed to be present, and the lower concentration value of the two isotopes is assigned the upper concentration limit for that particular PCB isomer group. The value is then flagged with the letter "i" indicating that a chemical interference has inflated the reported concentration. An example of a data print-out showing the PCB desorption curves may be seen in Figure A4.

Detection Limit

The PCB detection limit for the TAGA/ASTA technique is defined as being 3 times the standard deviation of the background signal observed at the PCB masses, divided by the appropriate calibration factors. Thus by definition, the detection limit depends on two important factors:

i) the sensitivity, which is a function of the probe adsorption efficiencies and the benzene chemical ionization rates.

ii) the level of the interferences (adsorbed compounds that have the same nominal ionic mass as the targeted PCBs in both upwind and downwind air samples). Interference

levels are highly variable depending on the sampling site, the source(s) in the immediate area, and the local meteorological conditions.

During a survey air samples are spiked periodically with 0.425 ug/m3 per PCB isomer group to establish the daily sensitivity factors and determine, on-site, the detection limits of the technique. Typical detection limits range from 0.01 to 0.05 ug/m3 per isomer group, or from 0.04 to 0.20 ug/m3 for total (di to pentachlorobiphenyls) PCBs, depending on the complexity of the sample matrix.

SUMMARY

The TAGA/ASTA PCB monitoring technique is a specialized application of the mobile TAGA 3000. It was developed to rapidly screen the ambient air for volatile PCBs. Important features of the technique to consider when assessing the data are:

1) The technique was developed to measure gas phase PCBs. (Should non-volatile PCBs be trapped by the probe they would be reported as volatile PCBs and included in the total amounts.)

2) PCB levels are determined continuously in 2 minute periods.

3) Four isomer groups are monitored simultaneously (normally the dichlorobiphenyls to pentachlorobiphenyls).

4) The detection limits for total PCBs typically range from 0.04 to 0.20 ug/m3 depending on the sample matrix.

In summation, the mobile TAGA/ASTA technique is a rapid screening method for volatile PCBs, providing near real-time detection at the time when PCBs are potentially released into the atmosphere. It is the only method currently available to the Ministry by which the ambient air can be instantaneously scanned for PCBs, providing valuable information, on-site.

TAGA 3000 SYSTEM

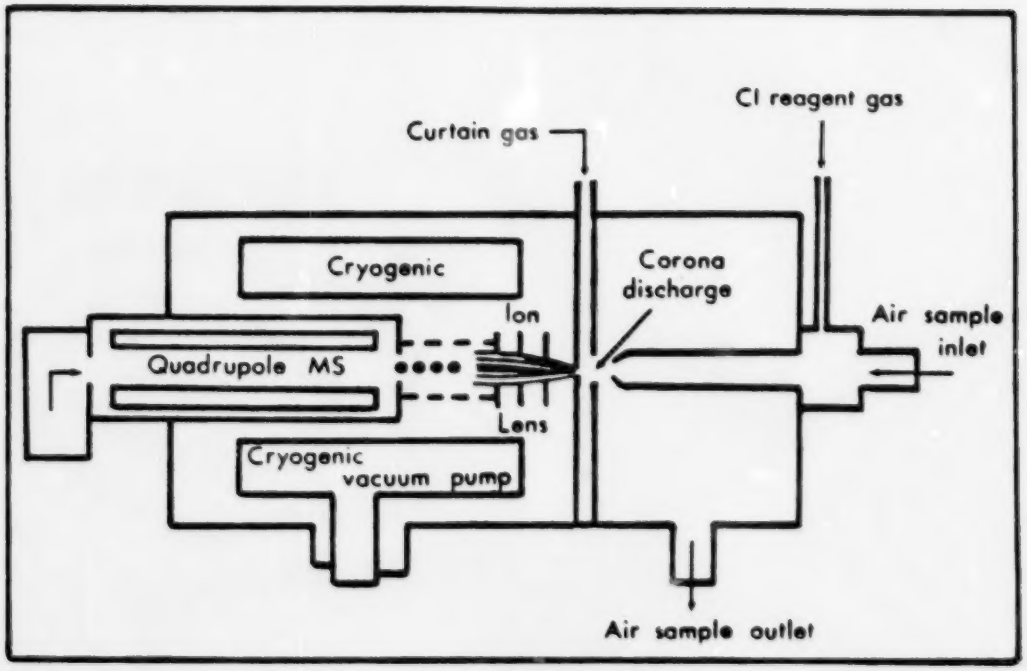


FIGURE A1: SCHEMATIC OF THE TAGA 3000 SYSTEM INSTALLED IN MAMU #3

ASTA SCHEMATIC

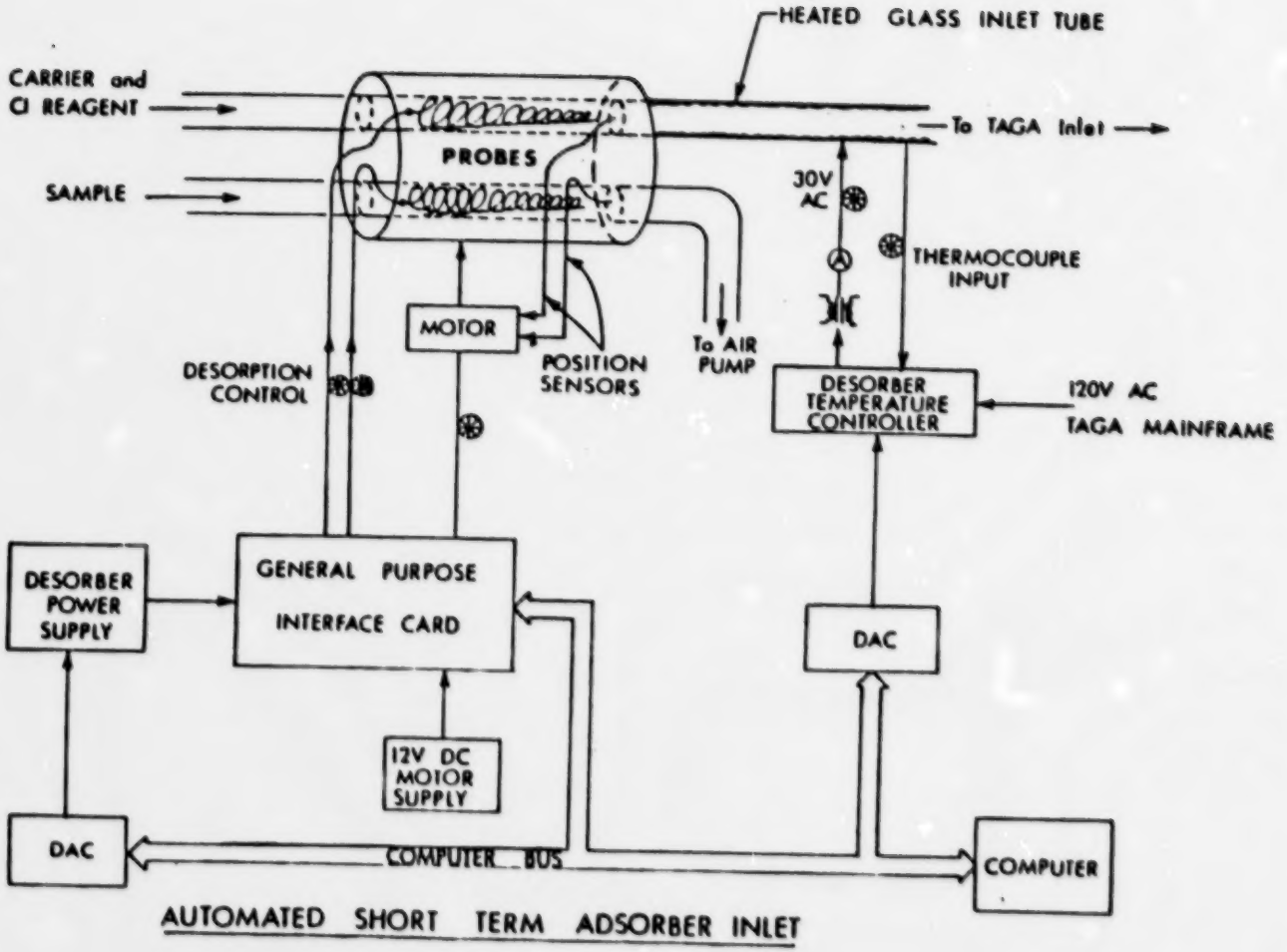


Figure A2: Schematic of the ASTA used in conjunction with the TAGA PCB Monitoring technique.

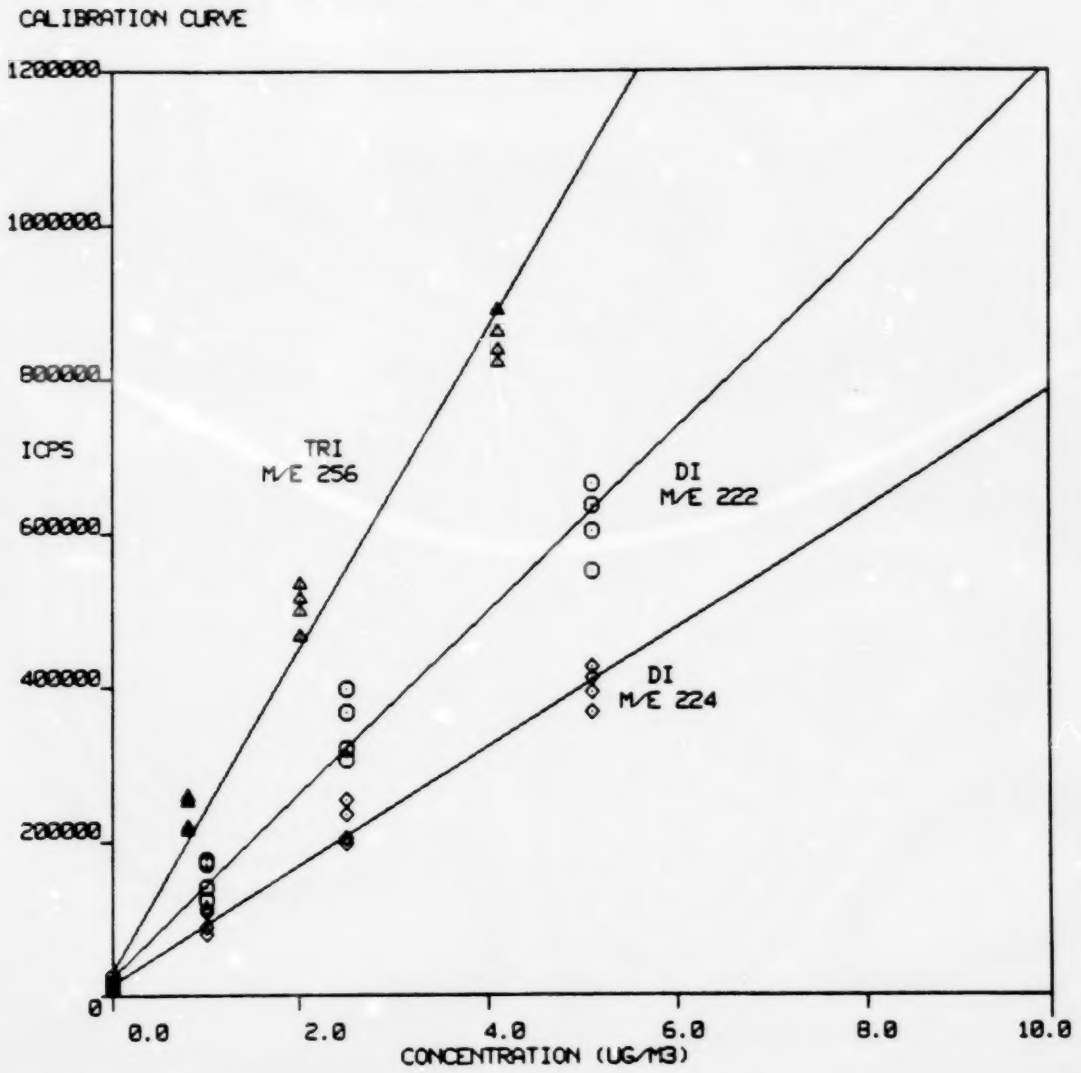
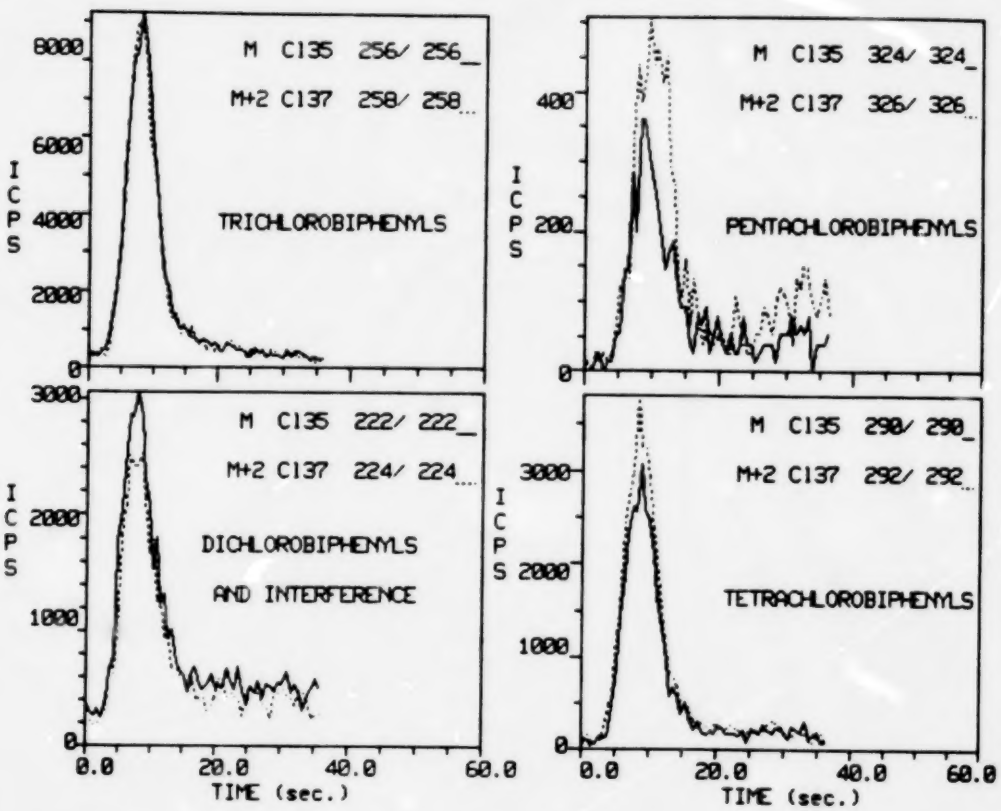


FIGURE A3: EXAMPLE OF CALIBRATION CURVE FOR DI AND TRICHLOROBIPHENYLS

TAGA/ASTA MONITORING TECHNIQUE



MP/MD	MAX.INT	TIM.MAX	INT.IONS	NET	CONC	RATIO TO MP/MD		THEOR.
222/ 222	3053.	8.40	17143.	14691.	0.39i	1.283	224/ 224	1.540
224/ 224	2520.	9.12	13994.	11452.	0.47i	0.780	222/ 222	0.650
256/ 256	9213.	8.56	46335.	43368.	0.60	1.056	258/ 258	1.030
258/ 258	8906.	8.64	43545.	41069.	0.62	0.947	256/ 256	0.975
290/ 290	3067.	9.36	14284.	12730.	0.23	0.818	292/ 292	0.769
292/ 292	3800.	8.80	17271.	15562.	0.23	1.222	290/ 290	1.300
324/ 324	360.	9.52	1707.	1303.	0.10	0.620	326/ 326	0.615
326/ 326	507.	10.24	2662.	2099.	0.11	1.612	324/ 324	1.626
					1.3			

FIGURE A4: Example of TAGA data print-out, PCB analysis. Concentrations are in units of ug/m3. Note the ratio for isotope 222/224 dichlorobiphenyl is mismatched, where "i" denotes a contribution by interference at masses 222 and/or 224. The total PCB level is computed to be 1.3 ug/m3.